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Final Report
by
J. Economy
High Performance Fibers
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Introduction and Background

A 2 1/2 year ONR/ARPA funded program to develop a low cost process for manufacture of a high strength/high modulus (σ/E) boron nitride (BN) fiber was initiated on 7/1/90 and ended on 12/31/92. The preparation of high σ/E BN fibers had been demonstrated in the late 1960's by the PI using a batch nitriding of B_2O_3 fiber with NH_3 followed by stress graphitization at ~2000°C. Such fibers displayed σ/E values comparable to PAN based carbon fibers but the mechanicals were variable most likely because of redeposition of volatiles at 2000°C. In addition, the cost of the fibers was very high due to the need for many hours of nitriding necessary to convert the B_2O_3 fibers. The use of batch nitriding negated two possible cost advantages of this concept, namely, the ease of drawing very fine, multi-filament yarn of B_2O_3 and more importantly the very low cost of the starting materials i.e. ~ 45¢/lb for H_3BO_3 and 11¢/lb for NH_3, ($1.25/lb total raw material costs). It should be noted that availability of a low cost, high σ/E BN fibers would not only afford cost advantages over current carbon fibers but would also open up new opportunities based on the improved oxidative resistance of BN over carbon (825°C vs 425°C), low dielectrics (stealth) and increased potential for design of metal and ceramic matrix composites (BN is far more stable than carbon to the high temperatures required for processing these composites).

The intent of this program was to draw much finer filaments of B_2O_3 with diameters of 3 μ (vs 7-8 μ used earlier) to permit continuous nitriding of large tows with a total nitriding time of minutes instead of 30-40 hrs used earlier. A second goal was to explore tensioning of the partially nitrided fibers in order to induce the desired orientation and stabilization of the BN at temperatures below 1100°C instead of the 2000°C used in the earlier studies. To facilitate this work and also accelerate scale-up, Owens Corning was provided financial support to pursue design and implementation of a continuous nitriding and tensioning process.

In mid 1991 a program was also initiated to develop a matrix based on BN for possible use in a wide range of high temperature composites. A completely new approach was designed using a low viscosity borazine oligomer which readily infiltrated a fiber lay-up. This part of the program turned out to be highly successful and a number of composites were prepared using high σ/E carbon fibers and various inorganic fibers each with a number of unique properties.

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BN Fiber Development

1. Melt Drawing of 3.5 µ B_2O_3 fibers. The OCF personnel demonstrated that continuous multi-filament strands (800 ends) of 3.5 µ B_2O_3 fibers could be prepared using a standard E glass melter/bushings. Glasses containing up to 1% SiO_2 or 1% Al_2O_3 were prepared and evaluated. No advantages were identified in nitriding or stabilizing of the BN fiber with the SiO_2 additive. The Al_2O_3 containing glasses could not be drawn due to devitrification of the glass. The tendency for electrostatic charge build-up during fiber drawing could be controlled by use of ionizers while dodecane was used to coat and protect the fibers against damage during handling.

2. Nitriding of B_2O_3 Fibers. Several interrelated problems were addressed simultaneously in this phase, namely a) to reduce the time of nitriding from many hours down to a few minutes, b) develop annealing conditions that yielded a stable BN structure (d_{002}~3.35Å), c) eliminate any tendency for redeposition of B_2O_3 on the BN fiber surface during stabilization and d) induce orientation in the BN structure through tensioning during nitriding. A four stage nitriding and annealing cycle which involved nitriding from 270°C to 850°C and annealing at 1050°C (total time 22 minutes) to achieve a BN fiber with the desired interlayer spacing was successfully demonstrated. It was shown that the deposits on the fiber surface could be eliminated by carrying out the annealing at temperatures below 1100°C. A small amount of tensioning was applied throughout the nitriding process leading to 4% elongation and some orientation corresponding to E values of ~10-15 m.s.i. Because of excessive handling of the fibers during the four stage process it was not possible to further optimize the orientation in the fiber.

3. Continuous Process for BN Fiber Manufacture. A continuous process for drawing 800 ends of B_2O_3 filaments and then nitriding a tow of combined 800 ends was installed at OCF during the Winter of 92/93. No attempt was made by OCF to exercise the system during the Spring of 1993 even though we obtained a no cost extension through June 1993, and spent considerable time with them to define conditions for continuous nitriding.

BN Matrix Development

1. Fabrication of Carbon Fiber/BN Matrix Composites (CF/BN). It was shown that CF/BN could be prepared using a specially designed borazine oligomer in one step (three day cycle) to achieve densities of 1.45 g/cc(1.60 g/cc using two steps). Typically C/C composite manufacture requires four to five reimpregnation plus a chemical vapor infiltration step with a cycle of several months. The CF/BN composites displayed significantly higher mechanicals than C/C and in one case flexural σ/E values comparable to rule of mixtures was observed. Oxidation resistance of CF/BN compared to C/C was increased from 425°C to 825°C.

2. Fabrication of Ceramic/BN Matrix Composites. Using the conditions for fabricating C/BN a number of different composites were prepared using FP(DuPont),

Nextel (MMM), Nicalon (Dow Corning) and Sumica (Sumitomo). The first two fibers showed some deterioration during processing at 1200°C while the Nicalon (SiC) and Sumica (Mullite) gave composites with acceptable mechanicals. The composite based on Sumica fibers displayed a dielectric constant of 7.7 while the Nextel composites had a dielectric constant of ~6.2.

3. Liquid Crystalline Phase in the Borazine Oligomer. Heating of the CF/BN (pitch based fibers) from 1200°C to 1500°C showed a major improvement in mechanicals. This could only be interpreted on the basis that the oligomers had a tendency to form a discotic phase which facilitated orientation at the fiber surface. Attempts to isolate such a phase were successful and X-Ray and optical data were obtained to corroborate presence of a liquid crystalline structure. There was some evidence that a certain percentage of this discotic/isotropic phase tended to form a highly crystalline BN on heating to temperatures of 500°C and below.

Conclusions

BN Fiber Program

1. Enough data are available to indicate feasibility of a continuous process for manufacture of a BN fiber. Potential to control degree of orientation and σ/E by tensioning is indicated but remains to be optimized. The ability to manufacture a low cost BN fiber appears possible but requires far more optimization of the nitriding under continuous operations.

2. Funding of OCF by UIUC to carry out the design of a continuous process proved to be unsatisfactory possibly because it did not represent a mainstream effort within OCF.

3. We have asked for and received the furnaces from OCF that were to be used in the continuous nitriding process. If this phase is reinitiated some time in the future some of the equipment will at least be available to accelerate start-up.

BN Matrix Program

1. This particular phase was highly successful in all aspects. In fact, a number of companies including aircraft brakes manufacturers, BN manufacturers and several companies involved with stealth and NASP have expressed strong interest in working with us to develop these composites.

2. Cost of the borazine used to prepare the oligomer represents a major barrier to commercialization (~$10,000/lb). We have recently established feasibility of one route with a cost of ~ $150/lb and are exploring a much lower cost route in the range of $10-20/lb.

3. The formation of a discotic oligomeric borazine appears to yield a stable BN at low temperatures (< 500°C) and could represent a major breakthrough in the formation of a wide range of BN shapes and coatings.